

**REDUCTION OF ARSENIC WASTES
IN THE
SEMICONDUCTOR INDUSTRY**

By
Joseph T. Swartzbaugh, Ph.D.
And
Jeffrey A. Sturgill

University of Dayton Research Institute
Environmental Science and Engineering Group
Dayton OH 45469-0132

Cooperative Agreement No. CR 821808-01

Project Officer
Paul Randall
Sustainable Technology Division
National Risk Management Research Laboratory
Cincinnati, Ohio 45268

**NATIONAL RISK MANAGEMENT RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268**

NOTICE

This publication was developed under Cooperative Agreement No. CR 821808-01 by the U.S. Environmental Protection Agency. EPA made comments and suggestions on the document intended to improve the scientific analysis and technical accuracy of the document. However, the views expressed in this document are those of the University of Dayton and EPA does not endorse any products or commercial services mentioned in this publication. This document is intended as advisory guidance only to the wood preserving industry in developing approaches to waste reduction. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

FOREWORD

The U. S. Environmental Protection Agency is charged by Congress with protecting the Nation's land air and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of our natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge data base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory is the Agency's center for investigation of technological and management approaches for reducing risks from threats to human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for the prevention and control of pollution to air, land, water and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

ABSTRACT

The research described in this report was aimed at initiating and developing processes and process modifications that could be incorporated into semiconductor manufacturing operations to accomplish pollution prevention, especially to accomplish significant reduction in the quantity of arsenic waste generated in that industry. The effort resulted in the development of processes for the recovery of both gallium and arsenic from gallium arsenide semiconductor crystal manufacturing. Recovery of materials from both solid and aqueous waste streams was achieved and the solids recovery process was demonstrated at an operating semiconductor manufacturing plant. The processes developed herein are applicable to other types of III-V semiconductor manufacturing, including indium phosphide, gallium phosphide and indium arsenide manufacturing.

The two processes developed include processes for recovery of materials from both solid and aqueous waste streams. The solid waste recovery process a thermal process for separation of gallium and arsenic from each other and from process contaminants with subsequent thermal refining of the captured gallium and arsenic. The aqueous waste recovery process incorporates sequential precipitation of the arsenic and gallium to allow for their recovery and reuse. This report was submitted in partial fulfillment of the requirements of Cooperative Agreement No. CR 821808-01

TABLE OF CONTENTS

<u>Section</u>	<u>Description</u>	<u>Page</u>
	Notice	ii
	Foreword	iii
	Abstract	iv
	Acknowledgements	x
1.0	Conclusions and Recommendations	1
2.0	Introduction	3
	2.1 Why Arsenic and Other Toxic Elements are Important in Semiconductor Device Manufacturing	
	2.2 "Strategic" Elements Used in Semi-conductor Devices	5
	2.3 General Summary of Manufacturing Processes for Compound Semiconductors	7
	2.4 Summary of Pollution Prevention Processes Developed Under This Grant	13
3.0	Recycling and Recovery of Materials from Solid GaAs Wastes	18
	3.1 Current Disposal/Recycling Methodology	18
	3.2 Recovery Process Development	19
	3.3 Prototype System	21
4.0	Recovery and Recycling of Gallium and Arsenic from Crystal Polishing Wastewaters	30
	4.1 Current Treatment Methodology	30
	4.2 Approach for Metals Recovery	32
	4.3 Methods for Arsenic Recovery	35
	4.4 Methods for Gallium Recovery	39
	4.5 Process for Recovery of Materials from Aqueous Waste	42
5.0	Economic Assessment	43
	5.1 Factors Affecting the Economics of GaAs and Other III-V Material Recovery Systems	
	5.2 Important Economic Factors for Solid and Aqueous Gallium Arsenide Recovery	45

TABLE OF CONTENTS (continued)

<u>Section</u>	<u>Description</u>	<u>Page</u>
5.3	Important Economic Factors for Solid and Aqueous Indium Phosphide Waste Recovery	45
5.4	Important Economic Factors for Recovery of Other III-V Compounds	46
5.5	Economic Factors for Recovery of Wastes from III-V Epitaxial Processes	46
5.6	Summary	46
References		48

LIST OF FIGURES

<u>Figure No.</u>	<u>Description</u>	<u>Page</u>
2.1	Process Flow Diagram for Compound Semiconductor Device Fabrication	8
3.1	Schematic of the Recovery Process for III-V Solid Wastes	21
3.2	Cross-section of Unit Operation 1 – Thermal Separation Furnace	22
3.3	Schematic of Existing Equipment for Low-Temperature Purification of Gallium	23
3.4	Schematic of Existing Equipment for Sublimation /Purification of Arsenic	24
3.5	EDS Analysis of Unreacted GaAs	25
3.6	EDS Analysis of Volatized Material	26
3.7	EDS Analysis of Residue	26
3.8	EDS Analysis of Volatile Material after 2-hour Run	26
3.9	Analysis of Residue from 1-hour Run with Continuous Evacuation	27
3.10	Analysis of Residue from 2-hour Run with Continuous Evacuation	27
3.11	SIMS Analysis of Pure Gallium Fraction Resulting from Thermal, Low-Pressure Recovery of GaAs	28
3.12	SIMS Analysis of Gallium “Slag” Resulting from Thermal, Low-Pressure Recovery of GaAs	29
4.1	Current Treatment Approach for GaAs Polishing Wastes	31
4.2	Comparison of Metal Arsenate Systems	36
4.3	Experimental Residual Concentrations of As as a Function of pH and Metal-Arsenate System at 25°C	37

LIST OF FIGURES (continued)

<u>Figure No.</u>	<u>Description</u>	<u>Page</u>
4.4	Experimental Residual Concentrations of As in Calcium Arsenate Precipitates as a Function of pH and Temperature	38
4.5	Measured Residual Ga Concentrations as a Function of Metal-Arsenate System and pH at 25°C	40
4.6	Measured Residual Ga Concentrations Following Calcium Arsenate Precipitation as a Function of Temperature and pH	41
4.7	Developed Process for the Sequential Recovery of Gallium and Arsenic from GaAs Polishing Wastes	42

LIST OF TABLES

<u>Table No.</u>	<u>Description</u>	<u>Page</u>
2-1	Compound Semiconductors	5
4-1	Arsenic and Gallium Concentrations in a Typical Industrial Filtrate and Filter Cake using Ferric Hydroxide Coprecipitation Methodology	31
4-2	Treatment/Recovery Procedures for As Considered and Tested in Phase I	33
4-3	Treatment/Recovery Procedures for Ga Considered and Tested in Phase I	34
4-4	Comparison of Metal-Arsenate Systems for As and Ga Removal/Recovery from GaAs Polishing Wastewaters at Different Metal-As Ratios	39
5-1	Estimated III-V Raw Material Costs	43
5-2	Estimated Annual Tonnage of Bulk III-V Crystals Produced in 1995 in the U.S.	44
5-3	Estimated Annual Costs of Raw Material Wasted in the Form of Solids from Gallium Arsenide Crystals	45
5-4	Estimated Annual Costs of Raw Material Wasted in the Form of Aqueous Streams from Gallium Arsenide	45
5-5	Estimated Annual Costs of Raw Material Losses in Epitaxial Growth Processes	46
5-6	Total Estimated Annual Dollar Value of Wasted Raw Materials from III-V Semiconductor Growth Operations	47

ACKNOWLEDGEMENTS

This research was performed under U.S. EPA Cooperative Agreement No. CR821808-01. The researchers would first like to thank the staff of the U.S. Environmental Protection Agency for the opportunity to perform this much-needed research in this vital industry. Special thanks go to Mr. Paul Randall, the EPA's technical monitor for his many useful suggestions and for his understanding and support during difficult phases of the effort. Thanks go also to Dr. Morris Young, president of American X-tal Technology (AXT) and to the staff at AXT for their help and input in this research effort. Finally, the help and guidance of Ms. Laura Rae of the U.S. Air Force Wright Laboratories, Materials Lab-Electromagnetic Materials and Mr. Bob Gedrich of the U.S. Navy Surface Warfare Center are appreciated.